

(12) UK Patent Application (19) GB (11) 2 123 014 A

(21) Application No 8308605
(22) Date of filing 26 Apr 1979
Date lodged 29 Mar 1983
(43) Application published
25 Jan 1984
(51) INT CL³
C08L 67/02 C08K 9/06
(52) Domestic classification
C3R 3C 3N1 3N2 C13X
C33B C5A C5B1 C6X C8R
L6F V
U1S 1384 3044 3052 C3R

(56) Documents cited
None

(58) Field of search
C3R
C3K

(60) Derived from Application
No. 7914500 under
Section 15(4) of the
Patents Act 1977

(71) Applicant
General Electric
Company,
(USA—New York),
1, River Road,
Schenectady 12305,
State of New York,
United States of America

(72) Inventors
Edwin Joseph Goedde,
Fred Frank Holub,
Phillip Steven Wilson

(74) Agent and/or address for
service
Michael Burnside and
Partners,
2, Serjeants' Inn,
Fleet Street,
London,
EC4Y 1HL

(54) Modified polyester
compositions

(57) Modified thermoplastic polyester
compositions are provided which
comprise (a) a poly(1,4-butylene
terephthalate) resin as the sole resin

component and (b) a modifier therefor
comprising a combination of an
amino-silane-treated clay and a
segmented copolyester. The modifiers
provide easier processability and
enhanced resistance to warpage in
articles molded from the
compositions.

GB 2 123 014 A

SPECIFICATION

Modified polyester compositions

This invention relates to modified thermoplastic polyester compositions which are more readily moldable to articles of improved dimensional stability. More particularly, the invention pertains to compositions of a poly(1,4-butylene terephthalate) resin which are modified with an effective amount of a certain filler polymer combination.

High molecular weight linear polyesters and copolyesters of glycols and terephthalic or isophthalic acid have been available for a number of years. These are described *inter alia* in U.S. Patents No. 2,465,319 and 3,047,539. These patents disclose that the polyesters are particularly advantageous as film and fiber formers.

Poly(1,4-butylene terephthalate), because of its very rapid crystallization from the melt, is uniquely useful as a component in injection moldable compositions. Workpieces molded from such polyester resins, in comparison with other thermoplastics, offer a high degree of surface hardness and abrasion resistance, high gloss, and lower surface friction.

It has now been discovered that poly(1,4-butylene terephthalate) can be greatly improved in processability and dimensional stability by intimately mixing it with a specific combination of modifiers.

According to this invention, there is provided a thermoplastic composition which comprises:

(a) a polyester composition consisting of a linear or branched poly(1,4-butylene terephthalate) resin as the sole resin component; and

(b) an amount up to 60 parts by weight, per 100 parts by weight of (a) and (b) combined, of a modifier therefor comprising a combination of aminosilane-treated clay and a segmented copolyester; the amount of modifier being sufficient to render the composition more readily moldable to articles of improved dimensional stability than articles omitting the modifier.

The compositions of the invention are useful for molding, e.g., injection molding, compression molding and transfer molding.

The polyester resins of the compositions of this invention are available commercially or can be prepared by known techniques such as by the alcoholysis of esters of terephthalic acid with butane diol and subsequent polymerization, by heating the glycol with the free acids or with halide derivatives thereof, and similar processes. These are described in U.S. Patents No. 2,465,319 and 3,047,539, and elsewhere.

Illustratively, these high molecular weight polyesters will have an intrinsic viscosity of at least 0.4 deciliters/gram and preferably, at least 0.6 deciliters/gram as measured in a 60:40 phenol/tetrachloroethane mixture at 30°C.

Especially useful when high melt strength is important are branched high melt viscosity poly(1,4-butylene terephthalate) resins, which include a small amount, e.g., up to 5 mole percent based on the terephthalate units, of a branching component containing at least three ester forming groups. The branching component can be one which provides branching in the acid unit portion of the polyester, or in the glycol unit portion, or it can be a hybrid. Illustrative of such branching components are tri- or tetracarboxylic acids, such as trimesic acid, pyromellitic acid, and lower alkyl esters thereof, or, preferably, polyols, and especially preferably, tetrols, such as pentaerythritol; triols, such as trimethylolpropane; or dihydroxy carboxylic acids and hydroxydicarboxylic acids and derivatives, such as dimethyl hydroxyterephthalate.

The branched poly(1,4-butylene terephthalate) resins and their preparation are described in U.S. Patent No. 3,953,404.

In certain preferred features the composition will include reinforcing fibrous (filamentous) glass. The filamentous glass to be employed as reinforcement in such embodiments of the present compositions is well known to those skilled in the art and is widely available from a number of manufacturers. For compositions ultimately to be employed for electrical uses, it is preferred to use fibrous glass filaments comprised of lime-aluminum borosilicate glass that is relatively soda free. This is known as "E" glass. However, other glasses are useful where electrical properties are not so important, e.g., the low soda glass known as "C" glass. The filaments are made by standard processes, e.g. by steam or air blowing, flame blowing and mechanical pulling. The preferred filaments for plastic reinforcement are made by mechanical pulling. The filament diameters range from 0.00012 to 0.00075 inch, but this is not critical to the present invention.

The length of the glass filaments and whether or not they are bundled into fibers and the fibers bundled in turn to yarns, ropes or rovings, or woven into mats, and the like, are also not critical to the invention. However, in preparing the molding compositions, it is convenient to use the filamentous glass in the form of chopped strands of from one-eighth to 2 inches long. In articles molded from the compositions, on the other hand, even shorter lengths will be encountered because, during compounding, considerable fragmentation will occur. This is desirable, however, because the best properties are exhibited by thermoplastic injection molded articles in which the filament lengths lie between 0.0005 and 0.250 inch.

The amount of the reinforcing glass can vary widely depending on the formulation and needs of the particular composition, it being essential only that an amount is selected which is at least sufficient

to provide reinforcement. Preferably, however, the reinforcing fibrous glass will comprise from 1 to 60% by weight of fibrous glass and (a) and (b), combined.

It has also been discovered that the polyester compositions of this invention which contain fibrous glass exhibit improved impact and flexural properties when the glass is predispersed in the resin.

It has further been found that even relatively minor amounts of the modifier (b) are effective in providing significant improvements in processability, etc. In general, however, the modifier (b) will be present in amounts of at least 1% by weight, preferably from 2.5 to 50% by weight, of (a) and (b). With amounts in excess of 50% by weight, some reduction in ease of processability may be experienced.

One component of modifier (b), the aminosilane-treated clay, can be made by treating finely divided reinforcing clay, e.g., kaolin clay, i.e., hydrophylic hydrous aluminum silicate, with an aminosilane. A preferred aminosilane-treated clay is made by reacting kaolin with γ -aminopropyl ethoxysilane.

The other component of modifier (b) is a segmented block copolyester, e.g., a block polybutylene-co-polypropylene glycol terephthalate resin. These are commercially available, e.g., Hytrel 4055 from DuPont Company, Wilmington, Del., U.S.A., ("Hytrel" is a Registered Trade Mark).

Other ingredients, such as dyes, pigments, flame retardants, and drip retardants can be added for their conventionally employed purposes.

The compositions of this invention can be prepared by a number of procedures. In one way, the modifier and any reinforcement, e.g., glass fibers is put into an extrusion compounder with the resinous components to produce molding pellets. The modifier, and reinforcement, if any, is dispersed in a matrix of the resin in the process. In another procedure, the modifier is mixed with the resins by dry blending, then either fluxed on a mill and comminuted, or they are extruded and chopped. The modifying agent can also be mixed with the resins and directly molded, e.g., by injection or transfer molding techniques.

It is always important thoroughly to free all of the ingredients; resin, modifier, reinforcement, if used, and any optional, conventional additives from as much water as possible.

In addition, compounding should be carried out to ensure that the residence time in the machine is short; the temperature is carefully controlled; the friction heat is utilized; and an intimate blend between the resin and the modifier is obtained.

Although it is not essential, best results are obtained if the ingredients are pre-compounded, pelletized and then molded. Pre-compounding can be carried out in conventional equipment. For example, after carefully pre-drying the polyester and modifier and the reinforcing agent, if used, e.g., under vacuum at 100°C for 12 hours, a single screw extruder is fed with a dry blend of the ingredients, the screw employed having a long transition section to ensure proper melting. On the other hand, a twin screw extrusion machine, e.g., a 28 mm Werner Pfleiderer machine can be fed with resin and additives at the feed port and reinforcement downstream. In either case, a generally suitable machine temperature will be 450 to 460°F.

The pre-compounded composition can be extruded and cut up into molding compounds such as conventional granules, pellets, etc., by standard techniques.

The composition can be molded in any equipment conventionally used for glass-filled thermoplastic compositions, e.g., a Newbury type injection molding machine with conventional cylinder temperatures, e.g., 450—525°F and conventional mold temperatures, e.g., 130—150°F.

The following examples illustrate the invention. They are set forth as a further description but are not to be construed as limiting the invention thereto.

Examples 1 to 8

Dry blends of poly(1,4-butylene terephthalate) resin (PBT), intrinsic viscosity 1.05 dl/g, melt viscosity 6,200 poise, aminosilane-treated clay, a segmented copolyester, and mold release/stabilizer are compounded and extruded at 520°F in an extruder. The extrudate is pelletized and injection molded at 520°F (mold temperature 130°F). The formulations and physical properties are shown in Table 1.

Tabl 1

Example Composition (parts by wt.)		1	2	3	4	
5	Poly(1,4-butylene terephthalate)	58	48	30	28	5
	30% Fibrous glass-filled poly(1,4-butylene terephthalate)	20	30	40	50	
10	γ -aminopropylsilane-treated clay	14	14	14	14	10
	Segmented copolyester	7	7	7	7	
	Fibrous glass	—	—	—	—	
Properties						
15	Heat distortion temp. at 264 psi, °F	318	300	340	350	15
	Warp at R.T., mm	<1	<1	<1	<1	
	Warp at 30 min. 350°F, mm	4	6	12	19	
	Notched Izod impact, ft.lbs./in. notch	1.3	1.4	1.4	1.7	20
20	Unnotched Izod impact, ft.lbs./in.	13.8	12.2	12.1	11.4	
	Flexural str., psi	14,700	16,700	17,500	19,000	
	Flexural mod., psi	491,000	609,000	604,000	716,000	

Table 1 (cont.)

Example Composition (parts by wt.)		5	6	7	8	
25	Poly(1,4-butylene terephthalate)	73	70	67	64	25
	30% Fibrous glass-filled poly(1,4-butylene terephthalate)	—	—	—	—	30
30	γ -aminopropylsilane-treated clay	14	14	14	14	
	Segmented copolyester	7	7	7	7	
35	Fibrous glass	6	9	12	15	35
Properties						
	Heat distortion temp. at 264 psi, °F	284	348	354	363	
	Warp at R.T., mm	1	6	6	13	
40	Warp at 30 min. 350°F mm	8	14	17	18	40
	Notched Izod impact, ft.lbs./in. notch	1.2	1.3	1.3	1.2	
	Unnotched Izod impact, ft.lbs./in.	12.3	9.6	9.3	9.1	
45	Flexural strength, psi	13,500	15,500	16,700	17,500	45

The compositions have low warp after molding and especially excellent impact strength. It can also be noted that pre-compounding the glass fibers into the polyester resin prior to blending (Examples 1 to 4) with the remaining ingredients leads to lower warpage and improved impact and flexural strengths.

50 Claims

1. A thermoplastic composition which comprises:

(a) a polyester composition consisting of a linear or branched poly(1,4-butylene terephthalate) resin as the sole resin component; and

(b) an amount up to 60 parts by weight, per 100 parts by weight of (a) and (b) combined, of a

55 modifier therefor comprising a combination of aminosilane-treated clay and a segmented copolyester; the amount of modifier being sufficient to render the composition more readily moldable to articles of improved dimensional stability than articles omitting the modifier.

2. A composition as claimed in Claim 1 wherein the amount of modifier (b) is at least 1.0% by weight of (a) and (b).
3. A composition as claimed in Claim 2 wherein the amount of modifier (b) is from 2.5 to 50% by weight of (a) and (b).
- 5 4. A composition as claimed in any preceding Claim which also includes from 1 to 60% by weight of reinforcing fibrous glass based on (a), (b) and said fibrous glass. 5
5. A thermoplastic composition as claimed in Claim 4 wherein said fibrous glass is pre-dispersed in component (a).
- 10 6. A composition as claimed in any preceding Claim wherein said polyester resin (a) has an intrinsic viscosity of at least 0.4 deciliters/gram when measured in a solution in a 60:40 mixture of phenol and trichloroethane at 30°C. 10
7. A composition as claimed in Claim 6 wherein said intrinsic viscosity is at least 0.6 deciliters per gram.
- 15 8. A composition as claimed in any preceding Claim wherein said branched poly(1,4-butylene terephthalate) resin is a high melt viscosity poly(1,4-butylene terephthalate) resin which includes a small amount of a branching component containing at least three ester forming groups. 15
9. A composition as claimed in Claim 1 and substantially as hereinbefore described with reference to any of Examples 1 to 8.